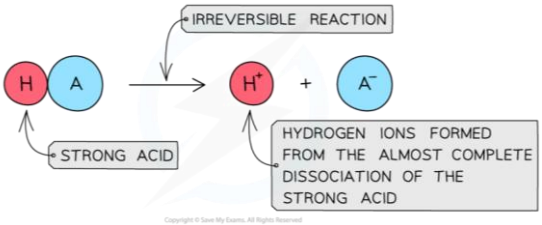
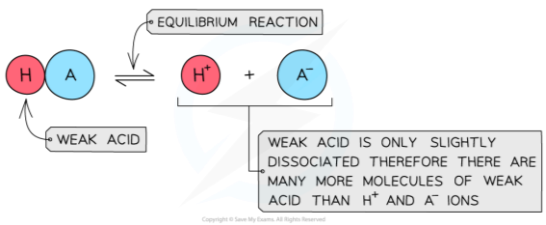
Topic 14: Acid-base Equilibria

Knowledge of the concepts introduced in Unit 2, Topic 9B Chemical Equilibria will be assumed and extended in this topic.

Students will be assessed on their ability to:

<table>
<tr><td>14.1</td><td>understand that a Brønsted–Lowry acid is a proton donor and a Brønsted–Lowry base is a proton acceptor and that acid-base reactions involve proton transfer</td></tr>
<tr><td></td><td>The Brønsted–Lowry theory defines:
An acid as a proton donor: HCl (aq) → H^+ (aq) + Cl^- (aq)
A base as a proton acceptor: OH^- (aq) + H^+ (aq) → H_2O (l)</td></tr>
<tr><td>14.2</td><td>be able to identify Brønsted–Lowry conjugate acid-base pairs</td></tr>
<tr><td></td><td>Conjugate acid-base pairs are a pair of reactants and products that are linked to each other by the transfer of a proton (one proton difference between the acid and base)
$HCl\ (g) + H_2O\ (l) \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$
acid base acid base
Each acid is linked to a conjugate base on the other side of the equation.
$HNO_3 + HNO_2 \rightleftharpoons NO_3^- + H_2NO_2^+$
Acid 1 Base 2 Base 1 Acid 2
$HCOOH + CH_3(CH_2)_2COOH \rightleftharpoons HCOO^- + CH_3(CH_2)_2COOH_2^+$
Acid 1 Base 2 Base 1 Acid 2
In these reactions, the substance with the bigger K_a will act as the acid</td></tr>
<tr><td>14.3</td><td>be able to define the term ‘pH’</td></tr>
<tr><td></td><td>Acidity of an aqueous solution depends on the number of H^+ ions in the solution
pH is defined as: $pH = -\log[H^+]$
The pH scale is a logarithmic scale with a base 10 meaning that each value is 10 times the value below it (pH 5 is 10 times more acidic than pH 6)</td></tr>
<tr><td>14.4</td><td>be able to calculate pH from hydrogen ion concentration</td></tr>
<tr><td></td><td>pH is defined as: $pH = -\log[H^+]$</td></tr>
<tr><td>14.5</td><td>be able to calculate the concentration of hydrogen ions in a solution, in mol dm^{-3}, from its pH, using the expression $[H^+] = 10^{-pH}$</td></tr>
<tr><td></td><td>Concentration of H^+ ions $[H^+] = 10^{-pH}$</td></tr>
<tr><td>14.6</td><td>understand the difference between a strong acid and a weak acid in terms of the degree of dissociation</td></tr>
<tr><td></td><td>
<table>
<tr><td>Strong acids
dissociate completely in aqueous sol.
Common eg: HCl (hydrochloric acid), HNO_3 (nitric acid) and H_2SO_4 (sulfuric acid)
Equilibrium position is to the far right</td><td>Weak acids
dissociate partially in aqueous solutions
Common eg: most organic acids, HCN (hydrocyanic acid), H_2S (hydrogen sulfide) and H_2CO_3 (carbonic acid)
Equilibrium position is more to the left</td></tr>
<tr><td> 
</td><td> 
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<tr><td>14.7</td><td>be able to calculate the pH of a strong acid</td></tr>
</table>

Calculating pH of a strong acid

Strong acids are completely ionized (completely dissociate) in solution

$HA\ (aq) \rightarrow H^+\ (aq) + A^-\ (aq)$

For (monoprotic) strong acids such as HCl and HNO_3,

The concentration of $[H^+]$ ions will be the same as the original concentration of the acid [HA] so we can assume that:

$[H^+] = [HA]$

(This is because the number of hydrogen ions formed from the ionisation of water is very small relative to the $[H^+]$ due to ionisation of strong acid and can therefore be neglected)

For strong acids, $pH = -\log[H^+]$ as the ions completely dissociate

For diprotic (dibasic) acids such as H_2SO_4,

Dibasic or diprotic acids have two replaceable protons and will react in a 1:2 ratio with bases

Diprotic acids dissociate in two steps: $\mathbf{H_2SO_4 \rightarrow HSO_4^- + H^+}$

$\mathbf{HSO_4^- \rightleftharpoons SO_4^{2-} + H^+}$

H_2SO_4 is a strong acid and so fully dissociates but HSO_4^- is a weak acid so only partially dissociates

(the contribution to the total $[H^+]$ from HSO_4^- ions is negligible as its dissociation is significantly reduced due to the abundance of H^+ ions from the first step, creating an equilibrium)

This means that the hydrogen ion concentration is less than double the acid concentration

14.8 be able to deduce the expression for the acid dissociation constant, K_a, for a weak acid

Always give pH values to 2 d.p. in the exam

For weak acids, we cannot use the above formula as there is a significant amount of acid that has not dissociated so we need to refer to the acid dissociation constant: K_a (mol/dm^3)

Let's consider HA to be an acid, then: $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Values of K_a are very small

When writing the equilibrium expression for weak acids, the following assumptions are made:

1. The concentration of hydrogen ions due to the dissociation of water is negligible $[H^+]$ is only due to dissociation of [HA] which means $[H^+] = [A^-]$
2. Dissociation of weak acid is negligible which means $[HA]_{start} = [HA]_{equilibrium}$

The value of K_a indicates the extent of dissociation

- The higher the value of K_a the more dissociated the acid and the stronger it is
- The lower the value of K_a the weaker the acid

14.9 be able to calculate the pH of a weak acid from K_a or pK_a values, making relevant assumptions

The range of values of K_a is very large and the values themselves are too small so we take log values of it as pK_a

$$pK_a = -\log(K_a)$$

Acid	K_a / mol dm^{-3}	pKa
Methanoic, HCOOH	1.77×10^{-4}	3.75
Ethanoic, CH_3COOH	1.74×10^{-5}	4.75
Benzoic, C_6H_5COOH	6.46×10^{-5}	4.18
Carbonic, H_2CO_3	4.30×10^{-7}	6.36

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Calculating pH of a weak acid

To make the calculation easier, two assumptions are made:

1) At equilibrium, $[H^+(aq)] = [A^-(aq)]$ as one molecule of HA dissociated into one of each ion
2) As the amount of dissociation is small, we can assume that the initial concentration of the undissociated acid has remained constant
   Hence, [HA(aq)] at equilibrium = [HA(aq)] at start

$$K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA\ (aq)]}$$

Simplifies to ↓

$$K_a = \frac{[H^+_{(aq)}]^2}{[HA_{(aq)}]_{initial}}$$

We can rearrange it to: $[H^+(aq)] = \sqrt{(K_a \times [HA(aq)])}$

$pH = -\log[H^+] = -\log\sqrt{(K_a \times [HA])}$

14.10 be able to define the ionic product of water, K_w

Dissociation of water is endothermic

In all aqueous solutions, an equilibrium exists in water where a few molecules dissociate into protons and hydroxide ions: $H_2O(aq) \rightleftharpoons H^+(aq) + OH^-(aq)$

Ionic product of water, K_w is the product of the concentration of the hydrogen ions and the hydroxide ions both measured in mol/dm^3

K_w is defined as: $K_w = [H^+(aq)][OH^-(aq)]$

The value of K_w at 298K (25°C) is always 1×10^{-14} mol^2 dm^{-6}

$[H^+]$	$[OH^-]$	Type of solution
0.1	1×10^{-13}	acidic
1×10^{-3}	1×10^{-11}	acidic
1×10^{-5}	1×10^{-9}	acidic
1×10^{-7}	1×10^{-7}	neutral
1×10^{-9}	1×10^{-5}	alkaline
1×10^{-11}	1×10^{-3}	alkaline
1×10^{-13}	0.1	alkaline

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When temperature changes (no longer 298K) pH also changes
An increase in temperature would shift the position of equilibrium to the right (as the forward reaction is endothermic) resulting in a larger $[H^+]$ and a lower pH

A neutral solution is one in which [H+] = $[OH^-]$

The relationship between K_w and pK_w is given by: $pK_w = -\log K_w$

14.11 be able to calculate the pH of a strong base from its concentration, using K_w or pK_w

Calculate the pH of a strong base

Strong bases such as NaOH are completely ionised in solutions

$BOH\ (aq) \rightarrow B^+\ (aq) + OH^-\ (aq)$

The concentration of $[OH^-]$ ions will be the same as the original concentration of the base [BOH] so we can assume that:

$[OH^-] = [BOH]$

(even strong alkalis have small amounts of H^+ ions which is due to the ionization of water)

$$[H^+] = \frac{K_w}{[OH^-]}$$

$$[H^+] = \frac{1 \times 10^{-14}}{[OH^-]}$$

$$pH = -\log[H^+] = -\log\left(\frac{1 \times 10^{-14}}{[OH^-]}\right)$$

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Diprotic base such as $Mg(OH)_2$

$[OH^-] = 2[Mg(OH)_2]$

14.12 be able to define the terms 'pK_a' and 'pK_w'

14.13

be able to analyse data from the following experiments:

i measuring the pH of a variety of substances, including equimolar solutions of strong and weak acids, strong and weak bases, and salts

ii comparing the pH of a strong and weak acid after dilution 10, 100 and 1000

i

Strong and weak acids

The relative strengths of different acids can be determined by measuring the pH of equimolar aqueous solutions of the acids, at the same temperature

The higher the value of the pH, the weaker the acid

FORMULA OF ACID	HCl	$CHCl_2COOH$	$CH_2ClCOOH$	HCOOH	CH_3COOH	CH_3CH_2COOH
pH OF 0.100 mol dm^{-3} AQUEOUS SOLUTION	1.00	1.14	1.93	2.38	2.87	2.93

decreasing acid strength

Strong and weak bases

The higher the value of the pH, the stronger the base

FORMULA OF BASE	NH_3	CH_3NH_2	$(CH_3)_2NH$	$CH_3CH_2NH_2$	$CH_3CH_2CH_2NH_2$	NaOH
pH OF 0.100 mol dm^{-3} AQUEOUS SOLUTION	11.13	11.82	11.83	11.84	11.86	13.00

increasing base strength

Salts

FORMULA OF SALT	NaCl	KNO_3	CH_3COONa	NH_4Cl	CH_3COONH_4
pH OF AQUEOUS SOLUTION	7.00	7.00	8.88	5.13	7.00

table C

The pH of NaCl is 7.00 because the salt is made from a strong acid (HCl) and a strong base (NaOH).

The same is true for KNO_3, which is a product of the strong acid HNO_3 and the strong base KOH.

An aqueous solution of CH_3COONa is alkaline because it is the product of a weak acid (CH_3COOH) and a strong base (NaOH).

An aqueous solution of NH_4Cl is acidic because it is the product of a strong acid (HCl) and a weak base (NH_3).

ii

Effect of dilution on the pH of aqueous solutions of acids

Strong acids

Because pH is a logarithmic scale, diluting a strong acid 10 times will increase its pH by one unit, and diluting it 100 times would increase its pH by two units

Earlier, we concluded that the concentration of H^+ ions from the dissociation of water in strong acids can be neglected but when it becomes too diluted, it can no longer be neglected as the contribution to the hydrogen ions from the water is now greater than that of acid

Weak acids

Weak acids would not change in the same way as when they are diluted

Diluting a weak acid 10 times will increase its pH by less than 1 unit (around 0.5)

Diluting a weak acid pushes the position of equilibrium to the right so the degree of dissociation increases and more H^+ ions are produced meaning pH increases but still less than expected

Proportion of acid molecules dissociating increases with dilution (for weak acids)

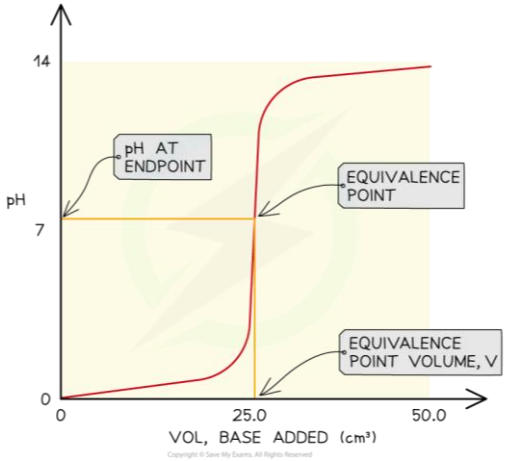
14.14

be able to calculate K_a for a weak acid from experimental data given the pH of a solution containing a known mass of acid

14.15

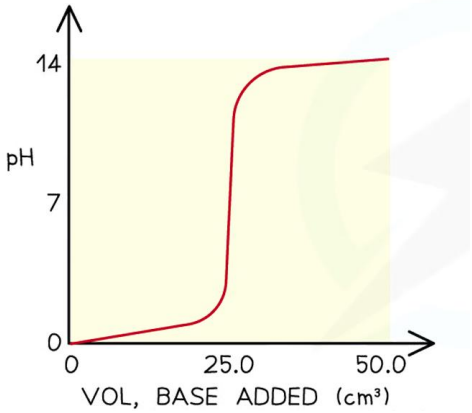
be able to draw and interpret titration curves, using all combinations of strong and weak monoprotic and diprotic acids with bases, and apply these principles to diprotic acids and bases

During a titration a pH meter can be used and a pH curve plotted

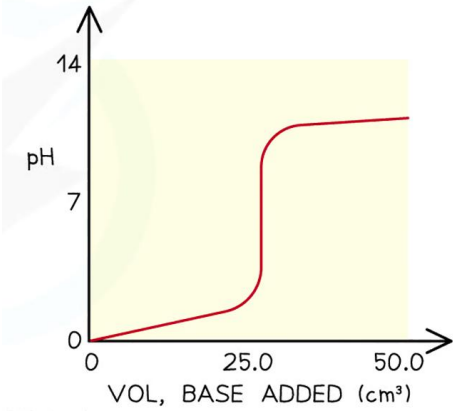


Note that endpoint does not always mean equivalence point: endpoint simply refers to when the indicator changes color while equivalence point is when acid and base have reacted in the exact proportions as dictated by the stoichiometric equation

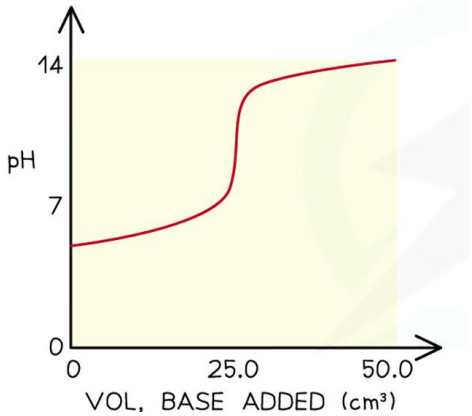
STRONG ACID + STRONG BASE



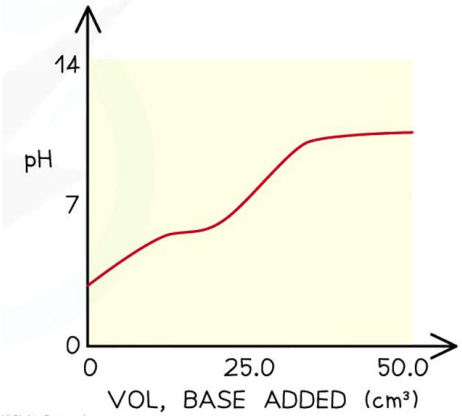
STRONG ACID + WEAK BASE



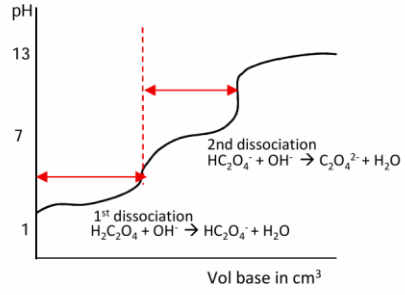
WEAK ACID + STRONG BASE



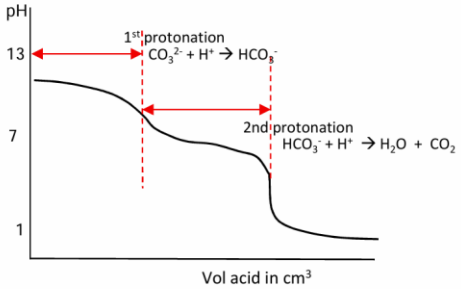
WEAK ACID + WEAK BASE



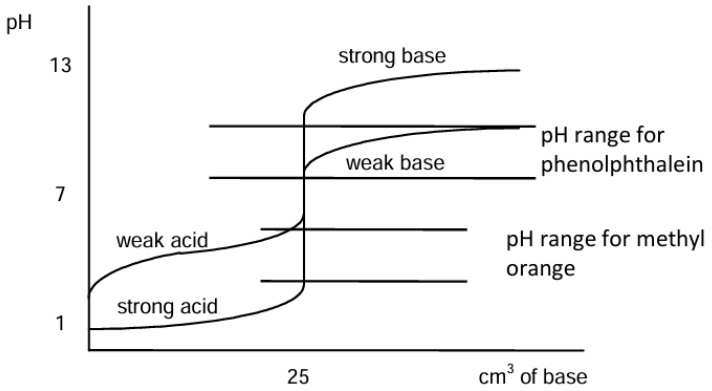
Diprotic acid with base



Diprotic base with acid



Diprotic acids will give a two part pH curve with two end points. Different indicators can be used to find out the two end points.

14.16	be able to select a suitable indicator for a titration, using a titration curve and appropriate data
	Constructing a pH curve 1. Transfer 25cm^3 of acid to a conical flask with a volumetric pipette 2. Measure initial pH of the acid with a pH meter 3. Add alkali in small amounts (2cm^3) noting the volume added 4. Stir mixture to equalise the pH 5. Measure and record the pH to 1 d.p. 6. Repeat steps 3-5 but when approaching endpoint add in smaller volumes of alkali 7. Add until alkali in excess **Calibrate** meter first by measuring known pH of a buffer solution. This is necessary because pH meters can lose accuracy on storage. Most pH probes are calibrated by putting probe in a set buffer (often pH 4) and pressing a calibration button/setting for that pH. Sometimes this is repeated with a second buffer at a different pH Can also improve accuracy by **maintaining** constant temperature
	Indicators behave like weak acids and form an equilibrium between two coloured species: HA(colour 1) ⇌ H + A (colour 2) The equilibrium constant for indicators is known as K_{In} (usually expressed in pK_{In}) The pH range of an indicator is a range of pH on either side of the pK_{In} value and different indicators change color over different ranges An indicator will work if the pH range of the indicator lies on the steep part of the titration curve The best indicator to choose is the one whose pK_{In} value is as close as possible to the pH at equivalence point  From this we can conclude that: **Phenolphthalein is used with strong bases** but not with weak bases **Methyl orange is used with strong acids** but not with weak acids
14.17	know what is meant by the term 'buffer solution'
	A **buffer solution** is a solution that minimizes the change in pH when a small amount of either acid or base is added An acidic buffer consists of a weak acid and its conjugate base (salt of that weak acid) A basic buffer consists of a weak base and its conjugate acid (salt of that weak base)
14.18	understand the action of a buffer solution
	Actions of a buffer! - A buffer solution will resist changes in pH so that the pH rises gradually as shown in the buffer region - A buffer solution is used to keep the pH almost constant - A buffer solution is formed from a weak acid and its salt or weak acid and a base - This produces a mixture of H^+ ions and OH^- ions which help resist change in pH

14.19	be able to calculate the pH of a buffer solution given appropriate data
	Calculate the pH of a buffer solution using the Hendersen-Hasselbalch equation ▪ To determine the pH, the concentration of **hydrogen ions** is needed which can be found using the equilibrium expression $K_a = \frac{[salt]\,[H^+]}{[acid]}$ which can be rearranged to $[H^+] = K_a \times \frac{[acid]}{[salt]}$ ▪ To simplify the calculations, **logarithms** are used such that the expression becomes: $-\log_{10}[H^+] = -\log_{10} K_a \times -\log_{10} \frac{[acid]}{[salt]}$ ▪ Since $-\log_{10}[H^+]$ = pH, the expression can also be rewritten as: $pH = pK_a + \log_{10} \frac{[salt]}{[acid]}$ ▪ This is known as the Hendersen-Hasselbalch equation
	Calculating the pH of a buffer solution **8** A buffer solution contains ethanoic acid, with a concentration of 0.10 mol dm^{-3}, and sodium ethanoate, with a concentration of 0.050 mol dm^{-3}. K_a for ethanoic acid = 1.7×10^{-5} mol dm^{-3} The pH of this buffer solution is ☒ **A** 2.88 ☒ **B** 4.47 ☒ **C** 4.77 ☒ **D** 5.07 $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (low conc. as dissociation of acid is almost negligible) $\therefore [CH_3COOH]_{at\ eqm} = [CH_3COOH]_{at\ start} = \frac{0.1}{2} = 0.08$ mol / dm^3 (this is because equal volumes of each solution (acid and salt) are mixed) $CH_3COONa \rightarrow CH_3COO^- + Na^+$ (high conc. as dissociation of salt is complete) $\therefore [CH_3COO^-]$ only comes from CH_3COONa (dissociation from acid is negligible) $\therefore [CH_3COO^-] = [CH_3COONa] = \frac{0.05}{2} = 0.026$ mol / dm^3 $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \Rightarrow [H^+] = 3.4 \times 10^{-5}$ $pH = -\log[H^+] = 4.47$ This method is still useful to know!
14.20	be able to calculate the concentrations of solutions required to prepare a buffer solution of a given pH

14.21	understand how to use a weak acid-strong base or strong acid-weak base titration curve to: i demonstrate buffer action ii determine K_a from the pH at the point where half the acid is neutralised/ equivalence point
i	The buffer region is indicated by a gradual change in pH (not STEEP) as the buffer solution resists changes in pH

	Ethanoic acid and sodium ethanoate CH_3COOH is a weak acid so only partially ionizes while CH_3COONa is a salt which fully ionizes in solution $CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq) + CH_3COO^-\ (aq)$ Ethanoic acid (high conc.) — ethanoate ion (low conc.) $CH_3COONa\ (s) + aq \rightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$ Sodium ethanoate (low conc.) — ethanoate ion (high conc.) There is a large reservoir of the undissociated acid and its conjugate base Both acid (due to partial ionization of ethanoic acid) and (due to full ionization of sodium ethanoate) are present in buffer in relatively high concentrations In the buffer solution, the ethanoic acid is in equilibrium with hydrogen and ethanoate ions $CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq) + CH_3COO^-\ (aq)$ (high conc.) (high conc.) **When H^+ ions are added**, The position of equilibrium shifts to the left as H^+ ions react with CH_3COO^- ions to form more CH_3COOH until equilibrium is re-established As there is a large reservoir of CH_3COO^- the concentration of CH_3COO^- in solution doesn't change significantly as it reacts with the added H^+ ions As there is a large reservoir of CH_3COOH the concentration of CH_3COOH in solution doesn't change significantly as CH_3COOH is formed from reaction of CH_3COO^- with H^+ Hence, ratio of $[CH_3COO^-]/[CH_3COOH]$ remains fairly constant and so does pH **When OH^- ions are added**, The position of equilibrium shifts to the right as the OH^- removes the H^+ by reacting with it to form water which means more CH_3COOH molecules ionise to form more H^+ and CH_3COO^- until equilibrium is re-established As there is a large reservoir of CH_3COO^- the concentration of CH_3COO^- in solution doesn't change significantly As there is a large reservoir of CH_3COOH the concentration of CH_3COOH in solution doesn't change significantly when CH_3COOH dissociates to form more H^+ ions Hence, ratio of $[CH_3COO^-]/[CH_3COOH]$ remains fairly constant and so does pH
ii	At **half equivalence** or half neutralization point, Volume of half-equivalence point = ½ Volume of equivalence point $[CH_3COOH(aq)] = [CH_3COO^-(aq)]$ pK_a = pH The equivalence point in a weak acid−strong base titration is above 7
14.22	understand the importance of buffer solutions in biological environments: i buffers in cells and in blood (H_2CO_3/HCO^-) ii in foods to prevent deterioration due to pH change (caused by bacterial or fungal activity)
14.23	**CORE PRACTICAL 11** **Finding the K_a value for a weak acid.**
	Further suggested practicals: i carry out the measuring of the pH of solutions mentioned in 14.13 ii obtain data to draw titration curves mentioned in 14.15 (which gives an opportunity to use data loggers) iii analysis of vinegar